Nitration spent acid is usually recovered by concentration.

Petroleum sludge acids may be blended with spent alkylation acid, thus supplying any fuel deficiency in the alkylation acid. Before processes were available for recovering alkylation spent acid (and before it was produced in large quantity), some petroleum sludges were recovered by diluting (hydrolyzing) them with water and increasing the temperature either at ambient or superatmospheric pressure. The hydrocarbon upper layer would then be decanted and the lower layer concentrated for acid recovery.

SULFUR POLLUTION

The reduction of pollution by sulfur and sulfur compounds has been extensively studied with the hope of eventual recovery for reuse.[30] Fuel desulfurization usually yields sulfur as hydrogen sulfide. Sulfur dioxide from nonferrous metal smelting or fuel combustion is most economically recovered as sulfuric acid, and less often as liquid sulfur dioxide, sulfur, or sulfate salts. Sulfuric acid has long been made from the richer gases at smelters with access to markets.

Large tonnages of sulfur are recovered from gaseous and light liquid petroleum fractions. In the United States, 23.4×10^6 t of sulfur dioxide is emitted from fuel combustion, compared with 2.3×10^6 recovered; 7.0×10^6 t is emitted from industrial processes, mainly smelting, compared with 0.8×10^6 recovered. Most of the sources are too small, too dilute, or too isolated for economical recovery. Nevertheless, new air pollution regulations are forcing smelters to recover up to 90 percent of input sulfur and are sharply limiting emissions of sulfur dioxide from fuel combustion. These regulations have brought about new facilities for desulfurizing fuel oils, a revived interest in low-sulfur liquid and gaseous fuels from coal, and many demonstration plants for removing sulfur dioxide from power plant waste gases.[31]

Emissions from new sulfuric acid plants are limited to 2 kg of sulfur dioxide and 75 g of acid mist per metric ton of acid made.

Recovery by the Claus process is never 100 percent because the reaction is an equilibrium one. Regulations controlling allowable emissions of sulfur dioxide from these plants vary from place to place and are often stricter than for larger plants. Many new plants are built with one more converter than is shown in Fig. 4 .2, and various tail gas cleanup units are being installed in both new and old plants.

Continuous copper smelters, such as the Outokumpu Oy, Mitsubishi, and Noranda processes, are being installed in order to recover high-strength sulfur dioxide gases suitable for efficient conversion into sulfuric acid, thus reducing atmospheric pollution.

Emissions from new installations of large coal-fired steam boilers are now limited to 516 g SO_2 per 1000 MJ of fuel burned. Usually the excess SO_2 is removed in tail gas scrubbers, and the resulting sulfates and/or sulfites are rejected without recovery of the sulfur values.

Pollution of streams and other sources of potable water is controlled by regulations limiting

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[30]Schuit and Gates, Chemistry and Engineering of Catalytic Hydrodesulfurization, *AIChE J.* **19** (3) 417 (1973); Semrau, Control of Sulfur Oxide Emissions form Primary Copper, Lead, and Zinc Smelters, *J. Air Pollut. Control Assoc.* **21** 185 (1971); Conn, Low BTU Gas for Power Plants, *Chem. Eng. Prog.* **69** (12) 56 (1973).

[31]Davis, Sulfur Dioxide Absorbed from Tail Gas with Sodium Sulfite, *Chem. Eng.* **78** (27) 43 (1971); Hyne, Methods for Desulfurization of Effluent Gas Streams, *Oil Gas J.* **70** (35) 64 (1972); Barry, Reduce Claus Sulfur Emissions, *Hydrocarbon Process.* **51** (4) 102 (1972); Chalmers. Citrate Process Ideal for Claus Tailgas Cleanup, *Hydrocarbon Process.* **53** (4) 75 (1974).

acidity, turbidity, oxygen demand, etc. Discharge of any liquid, gaseous, or solid waste is regulated by federal and local laws which require careful observance. For each particular application, permits to discharge must be obtained, often with great difficulty and at considerable expense.

CONCENTRATION

The literature describes various types of concentrators for sulfuric acid. Weak acid can be concentrated to a somewhat higher strength by immersing a steam-heated lead coil in a lead- or lead-and-brick–lined tank. Strong (98%) acid can be obtained by underfiring cast iron pots. The pots are not corroded provided that the acid is kept strong enough. Most concentration of acid today is accomplished in hot air blown concentrators or in vacuum concentrators using steam or other heat transfer fluids.

An air-blown concentrator[32] is shown in Fig. 4 .9. The burner supplies hot gases at about

[32]Duecker and West, op. cit., p. 340; Smith and Mantius, The Concentration of Sulfuric Acid, *Chem. Eng. Prog.* 78 (2) 78 (1978); Rodger, Developments in the Concentration of Sulfuric Acid, *Chem. Eng. Prog.* 78 (2) 39 (1982).
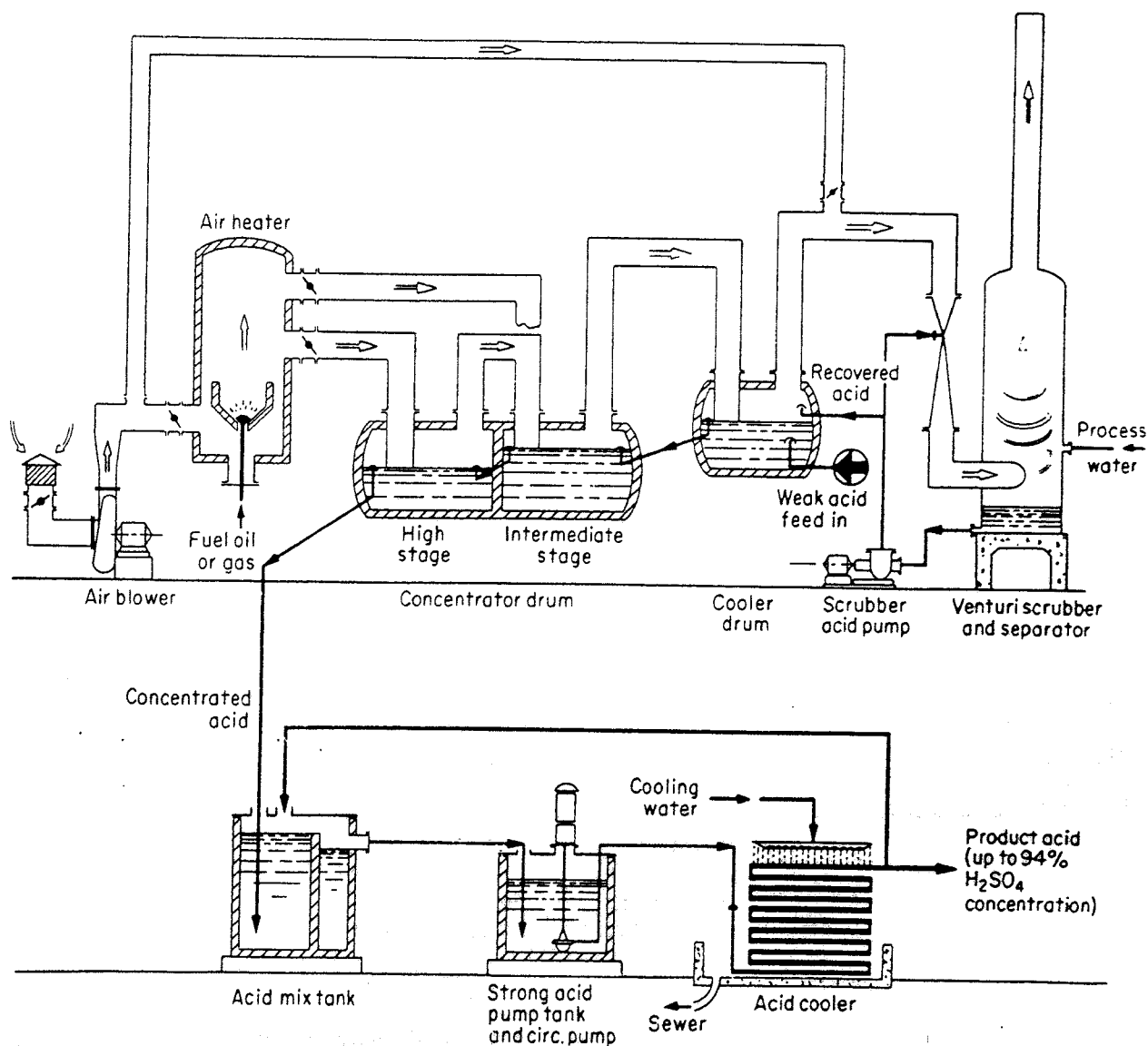

Fig. 4 .9. Flowchart for Chemico Drum sulfuric acid concentration process. *(Barnard and Burk Group.)*

680°C by the combustion of oil or fuel gas. These hot combustion gases are blown counter-current to the sulfuric acid in two compartments in the concentrating drum and remove water as they bubble through the acid. The off gases at 230 to 250°C from the first compartment of the drum pass to the second compartment, along with a portion of the hot gases from the combustion furnace. They leave at 170 to 180°C to enter a gas-cooling drum, where they are cooled to 100 to 125°C in raising the dilute acid to its boiling point. Since some sulfuric acid is entrained as a mist, the hot gases are passed through a venturi scrubber and a cyclone separator and are washed with feed acid or water for removal of the acid mist before discharge to the atmosphere. This reduces the acid mist to perhaps 35 mg/m^3 and involves considerably less capital investment than an electrostatic mist precipitator. This procedure gives an acid with a final concentration of 93% or just slightly higher. The hot gases, aided by the oxidizing action of the hot sulfuric acid, also burn out many impurities that may be found in spent acid being concentrated. Such air-blown concentrators are, therefore, extensively employed in the concentration of spent nitrating acid from munition works. If spent acid from petroleum purification is being handled, the flow of acid from the rear to the front compartment passes through an intermediate storage tank, where a skimmer removes some of the nonvolatile carbonaceous impurities. The concentrating compartments of the steel drum are lined with lead and acid-proof masonry. In this type of concentrator, the boiling
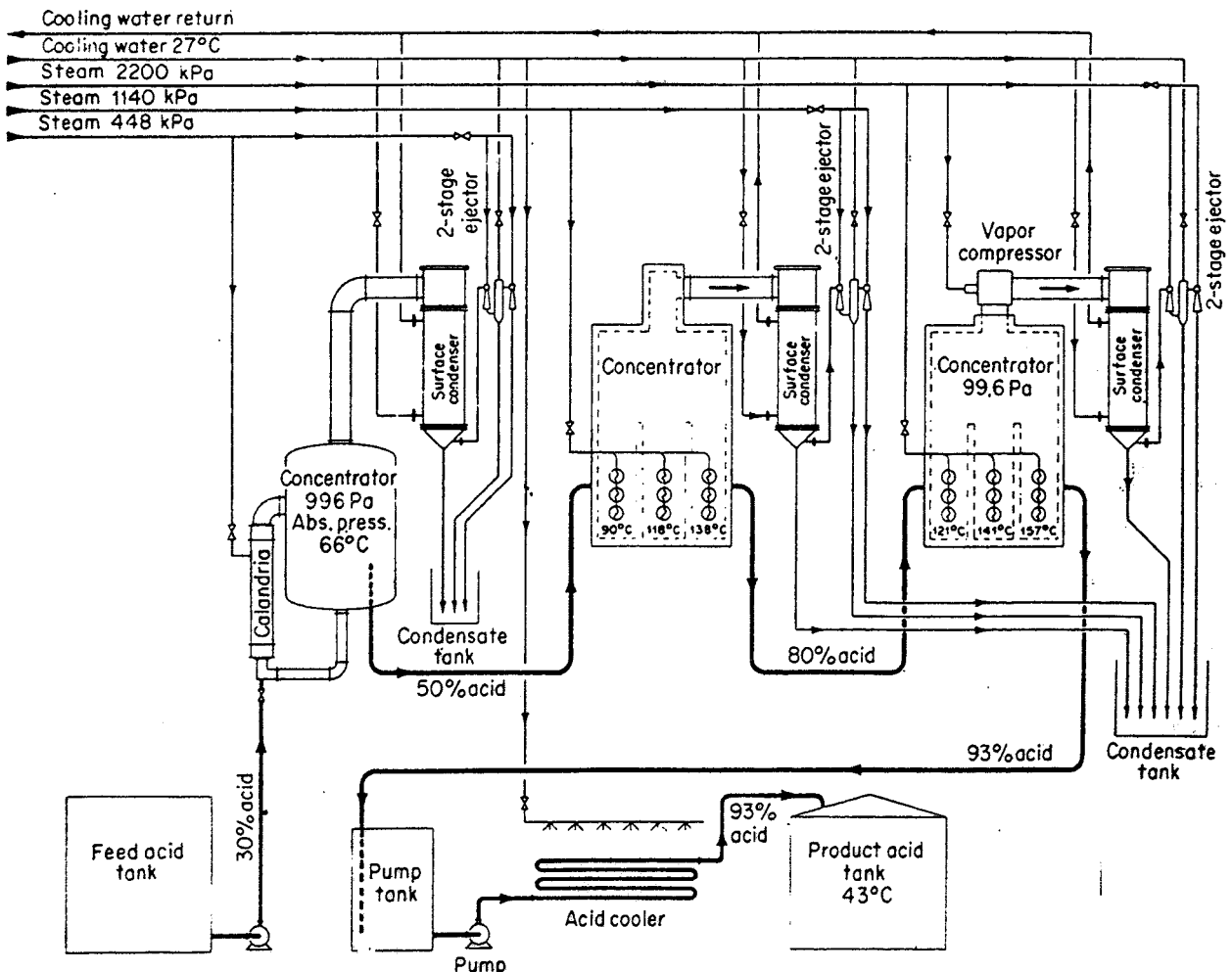

Fig. 4.10. Flowchart for Simonson-Mantius (SM) vacuum sulfuric acid concentration process. *(Barnard and Burk Group.)*

point of the acid is reduced as much as 60°C for 93% acid by the effect of hot air in reducing the partial pressure of the water vapor above the acid.

Simonson-Mantius[33] vacuum concentrators operate at pressures as low as 675 Pa and have long been used to concentrate sulfuric acid up to a maximum strength of 93%. Several types fit different conditions and various concentrations. The SM (formerly Simonson-Mantius) vacuum concentration process uses steam in tantalum indirect heaters to vaporize water from the acid that is maintained under vacuum. The use of vacuum lowers the boiling point of the acid. Any noxious vapors that are carried out of the concentrators are removed in the condensers. No acid fumes or mist escape to the atmosphere. Figure 4.10 shows a simplified flowchart for a standard SM unit.

Both the Chemico drum concentrator and the SM concentrator are now offered by Barnard and Burk of Mountainside, N.J.

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[33]Burke and Mantius, Concentration of Sulfuric Acid Under Vacuum, *Chem. Eng. Prog.* 43 237 (1947); see also Duecker and West, op. cit., pp. 329 and 335.

Chapter 5

Hydrochloric Acid and Miscellaneous Inorganic Chemicals

HYDROCHLORIC OR MURIATIC ACID

Hydrochloric acid, although not manufactured in such large quantities as sulfuric acid. is an important heavy chemical. Manufacturing techniques have changed. and some is made by the burning of chlorine in hydrogen.

Hydrogen chloride (HCl) is a gas at ordinary temperature and pressure. Aqueous solutions of it are known as *hydrochloric acid* or, if the HCl in solution is of the commercial grade, as *muriatic acid*. The common acids of commerce are 18°Bé (1.142 sp gr) or 27.9% HCl, 20°Bé (1.160 sp gr) or 31.5% HCl, and 22°Bé (1.179 sp gr) or 35.2% HCl,[1] which sell for $35, $55, and $63 per ton, respectively, on the east coast. Anhydrous HCl is available in steel cylinders at a very considerable increase in cost because of the cylinder expense involved.

HISTORICAL. Hydrogen chloride was discovered in the fifteenth century by Basilius Valentinius. Commercial production of hydrochloric acid began in England when legislation was passed prohibiting the indiscriminate discharge of hydrogen chloride into the atmosphere. This legislation forced manufacturers using the Leblanc process for soda ash to absorb the waste hydrogen chloride in water. As more uses for hydrochloric acid were discovered, plants were built solely for its production.

USES AND ECONOMICS. The largest users of hydrochloric acid are the metal, chemical, food, and petroleum industries. Industry experts estimate that the metal industries consume about 47 percent of the acid sold. A breakdown of the remaining uses is: chemical and pharmaceutical manufacturing and processing, 33 percent; food processing, 7 percent; oil well acidizing, 6 percent; and miscellaneous uses, 7 percent.

The major use of hydrochloric acid is in steel pickling (surface treatment to remove mill scale). Prior to 1963 almost all steel was pickled with sulfuric acid. Hydrochloric acid has taken over this market because it reacts faster than sulfuric with mill scale, less base metal is attacked by it, the pickled steel has a better surface for subsequent coating or plating operations, and much smaller quantities of waste pickle liquor are produced.

MANUFACTURE. Hydrochloric acid is obtained from four major sources: as a by-product in the chlorination of both aromatic and aliphatic hydrocarbons, from reacting salt and sulfuric

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[1]*Chem. Mark. Rep.* May 17, 1982.

acid, from the combustion of hydrogen and chlorine, and from Hargreaves-type operations ($4NaCl + 2SO_2 + O_2 + 2H_2O \rightarrow 2Na_2SO_4 + 4HCl$). As can be seen from Table 5.1. by-product operations furnish nearly 90 percent of the acid. The old salt–sulfuric acid method and the newer combustion method supply most of the remainder. The Hargreaves process is used by only one company.

Reactions and Energy Requirements. The basic steps in the production of by-product acid include the removal of any unchlorinated hydrocarbon, followed by the absorption of the hydrogen chloride in water. A typical chlorination, for illustration, is:

$$C_6H_6 + Cl_2 \longrightarrow C_6H_5Cl + HCl$$
$$\underset{\text{Benzene}}{} \qquad \underset{\text{Chlorobenzene}}{}$$
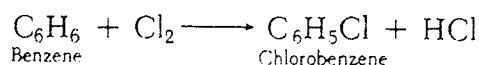
Since the chlorination of aliphatic and aromatic hydrocarbons evolves large amounts of heat. special equipment is necessary for control of the temperature of reaction.

The synthetic process[2] generates hydrogen chloride by burning chlorine in hydrogen. The purity of the ensuing acid is dependent upon the purity of the hydrogen and chlorine. As both of these gases are available in a very pure state as by-products of the electrolytic process for caustic soda, this synthetic method produces the purest hydrogen chloride of all of the processes.

The reaction between hydrogen and chlorine is highly exothermic and spontaneously goes to completion as soon as it is initiated. The equilibrium mixture contains about 4% by volume free chlorine. As the gases are cooled the free chlorine and free hydrogen combine rapidly so that when 200°C is reached the gas is almost pure HCl. By carefully controlling the operating conditions, a manufacturer can obtain a gas containing 99% HCl. The HCl gas is further purified by absorbing it in water in a tantalum or impervious or impregnated graphite absorber. The aqueous solution is stripped of hydrogen chloride under slight pressure, giving strong gaseous hydrogen chloride which is dehydrated to 99.5% hydrogen chloride by cooling it to −12°C. Large amounts of anhydrous hydrogen chloride are needed for preparing methyl chloride, ethyl chloride, vinyl chloride, and other such compounds.

Hydrochloric acid is extremely corrosive to most metals, and great care must be taken to choose the proper materials for plant construction. Water absorption of the hydrogen chloride made by any of the processes liberates about 1625 kJ/kg of hydrogen chloride absorbed. This heat[3] must be taken away in the absorber, or the efficiency will be low. Figure 5.2 illustrates the design of an absorber made from graphite.

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[2]ECT, 3d ed., vol. 12, 1980, p. 983.

[3]Naidel, Hydrogen Chloride Production in Graphite Vessels, *Chem. Eng. Prog.* 69 (2) 53 (1973); Hulswitt, Adiabatic and Falling Film Absorption of Hydrogen Chloride, *Chem. Eng. Prog.* 69 (2) 50 (1973).

Table 5.1 U.S. Production of Hydrochloric Acid
(in thousands of metric tons)

Source	1950	1960	1970	1978	1981
Salt and sulfuric acid	148	82	113	86	80
Chlorine and hydrogen	100	133	85	161	212
By-product and other	308	658	1614	2245	2042
Total	556	873	1812	2492	2334

SOURCE: U.S. Bureau of the Census

Blow-down line

Diabon
bursting
disk

Gas cooler

HCl

Cooling water

Chlorine
combustion
furnace

Pilot light
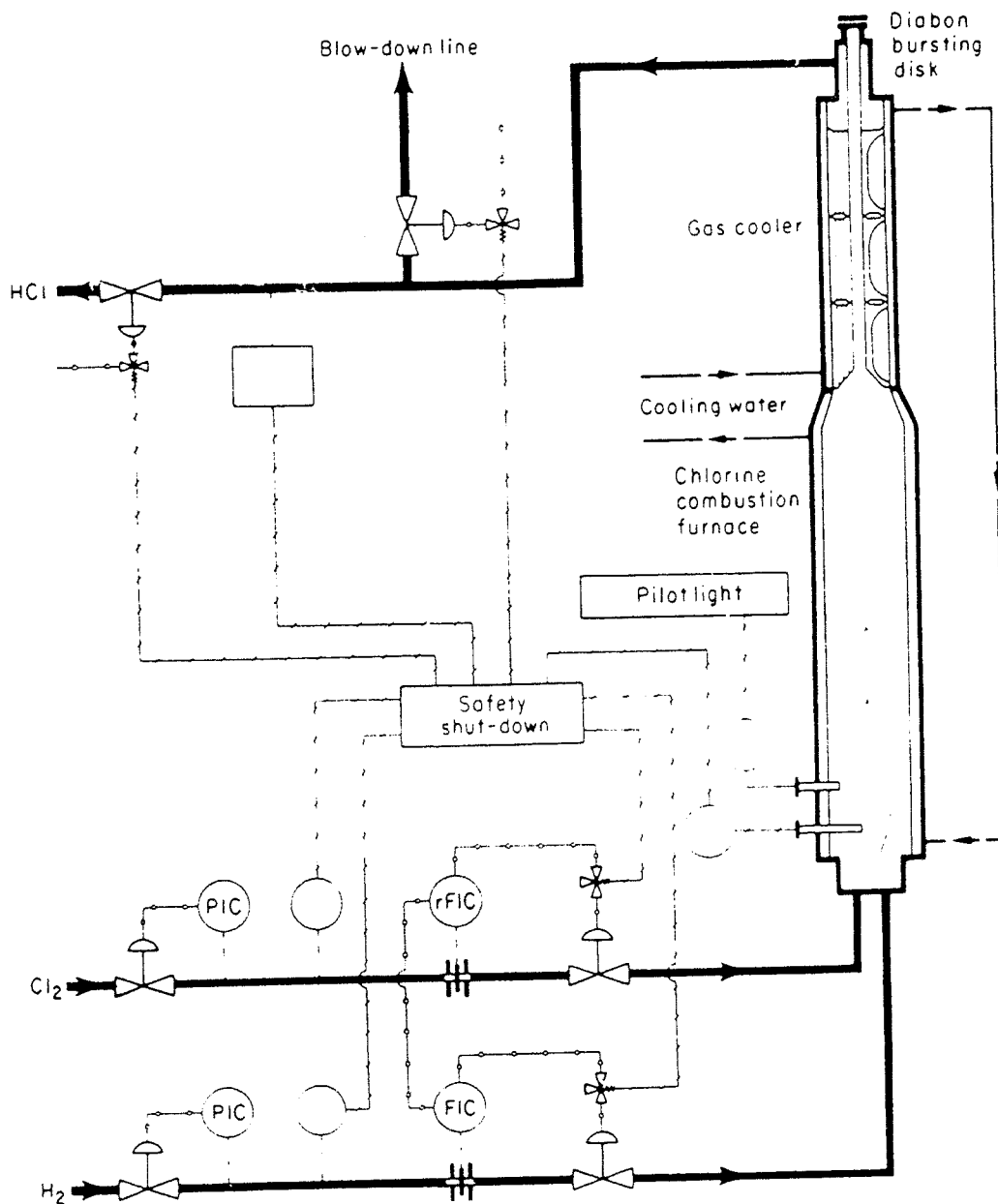
Safety
shut-down

PIC

rFIC

Cl₂

PIC

FIC

H₂

Fig. 5 .1. Chlorine combustion furnace. *(SIGRI Elektrographit GMBH.)*

BROMINE

Bromine is a member of the halogen family and is a heavy, dark-red liquid. It is much less common and more expensive than chlorine.

HISTORICAL. In 1824, 15 years after the discovery of iodine, bromine was discovered by Balard, a French chemist, who obtained it from mother liquor left after separating salt from seawater by evaporation. Its manufacture from the Stassfurt deposits of carnallite was begun in 1865, from the $MgBr_2$ in the liquors left after working up $MgCl_2$ and KCl. Today Ethyl Dow operates the largest plant at Freeport, Tex. (Fig. 5.3.), built during World War II.

USES AND ECONOMICS. About 60 percent of the domestic bromine output is used in the manufacture of ethylene dibromide for antiknock fluids.[4] This bromine compound prevents

[4]*Chem. Week* 127 (6) 53 (1980); 128 (12) 26 (1981); *Chem. Mark. Rep.* April 26, 1982; *Chem. Bus.* p. 24. May 3. 1982.
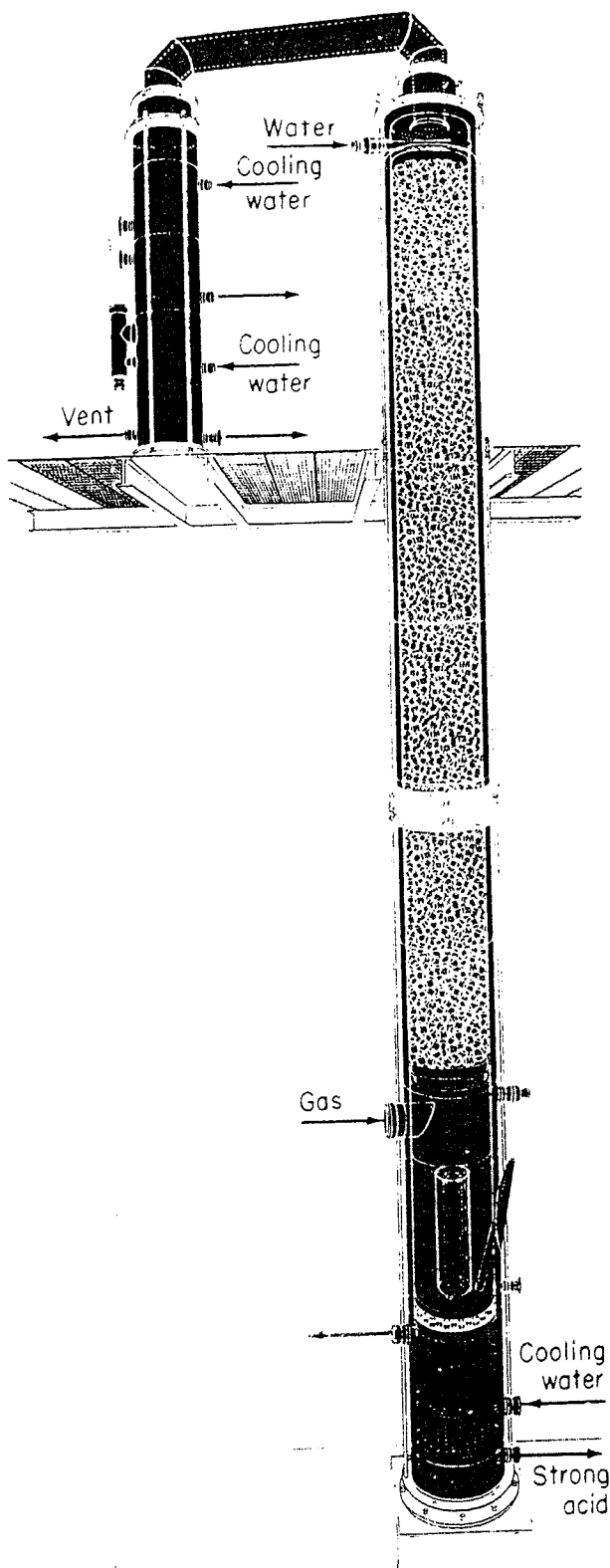
Fig. 5 .2. Diagram of an all-carbon (Diabon) hydrochloric acid, adiabatic absorption tower and cooler. *(SIGRI Elektrographit GMBH.)*

lead oxide deposits in engines which would otherwise result from tetraethyllead (TEL). The appearance of compact cars and jet-fuel airplanes has interrupted TEL and ethylene dibromide production. The Clean Air Act of 1970 mandated air quality standards that caused the EPA to make a commitment to eliminate 60 to 65 percent of lead antiknock compounds from gasoline by 1979. This further reduced the amount of bromine used by the gasoline industry. In 1981 only 40 percent of domestic production was consumed as ethylene dibromide.

Other bromine uses, however, have increased; most of this bromine is converted into organic or inorganic compounds. Although the demand for bromine in liquid form was lim-
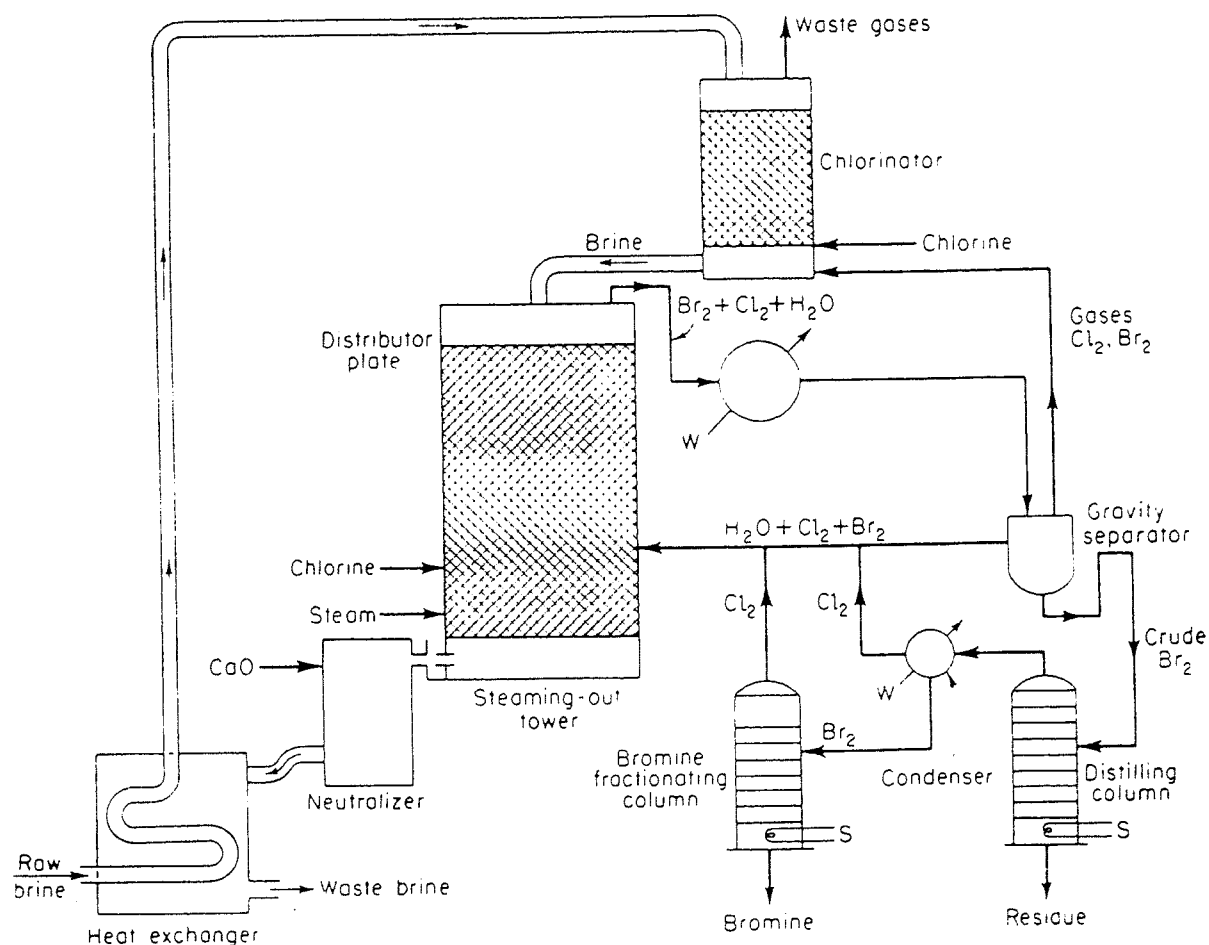
Fig. 5.3. Steaming-out process for bromine manufacture

ited mostly to laboratory reagents and small specialty uses, there is current interest in its use in swimming pools. Less than 1 ppm of bromine sterilizes the water without eye irritation or objectionable odor. Among the major inorganic compounds are alkali bromides, which are widely employed in photography and as comparatively safe sedatives in medicine. Metallic bromides are used for completion fluids in oil drilling muds and now account for nearly 20 percent of bromine production.

Hydrobromic acid resembles hydrochloric acid but is a more effective solvent for ore minerals, i.e., it has a higher boiling point and stronger reducing action. Methyl bromide (used as an insecticide, rodenticide, and methylating agent) and bromoindigo dyes are important organic compounds. Both methyl bromide and ethylene dibromide are finding growing use as soil and seed fumigants. Ethyl bromide is employed mainly as an ethylating agent in the synthesis of pharmacuticals (Chap. 40). Bromine is also employed in the preparation of dyes, disinfectants, flameproofing agents, and fire-extinguishing compounds. Flame retardants have been the biggest gainers among the newer uses. As flame-retardant standards become more strict, bromine products gain an increasing share of the market. In 1981 25 percent of bromine was used to produce flame retardants (Chap. 1). A promising new use is in the automobile sealed-beam headlight, which uses a bromine- or iodine-plus-tungsten element in an all-plastic unit. The halogen bulb emits a brigher, whiter light and has a 25 percent greater effective visibility distance than the usual all-glass unit.[5] Prior to World War I, Germany supplied approximately three-quarters of the total world production (1125 t).[5a] By 1929 the

[5]*Mater. Eng.* 92 (5) 36 (1980).

[5a]t = 1000 kg.

total U.S. production was 2886 t plus 7.65 t was imported. Since 1938 no imports have been received. In 1952, 70,290 t (value $30 million) was produced in this country, and by 1981 approximately 170,000 t was produced. The price of bromine in May, 1982 was 55 to 66 cents per kilogram in bulk and $1.90 per kilogram in drums. The United States is the world's largest producer and Israel is second, followed by the United Kingdom and West Germany.

MANUFACTURE. In the United States the chief raw material is seawater, in which bromine occurs in concentrations of 60 to 70 ppm. It is also manufactured from natural brines, where its concentration may be as high as 1300 ppm. In Germany it is produced from waste liquors resulting from the extraction of potash salts from the Stassfurt carnallite deposits, formerly the world's chief source of bromine. Various other countries have the following sources. Italy extracts bromine from one of its largest inland lakes; the U.S.S.R., from the water of Saksky Lake in Crimea; France, from deposits in Alsace; and Israel, from the Dead Sea, the richest source known.

Bromine from Seawater.[6]   A process was worked out for the removal of a small quantity of bromine by air-blowing it out of chlorinated seawater according to the equation

$$2NaBr + Cl_2 \rightarrow 2NaCl + Br_2\uparrow$$
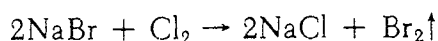
Manufacture from Salt Brines.[7]   In ocean water, where the concentration of bromine is relatively dilute, air has proved to be the most economical blowing-out agent. However, in the treatment of relatively rich bromine sources such as brines, *steaming out* the bromine vapor is the more satisfactory (Fig. 5.3). The original steaming-out process was developed by the Germans for processing the Stassfurt deposits, and with modifications is still used there, as well as in Israel and in this country. This process involves preheating the brine to 90°C in a heat exchanger and passing it down a chlorinator tower. After partial chlorination, the brine flows into a steaming-out tower, where steam is injected at the bottom and the remaining chlorine is introduced. The halogen-containing vapor is condensed and gravity-separated. The top water-halogen layer is returned to the steaming-out tower, and the crude halogen (predominantly bromine) bottom layer is separated and purified. *Crude bromine* from any of the foregoing processes can be purified by redistillation or by passing the vapors over iron filings which hold back the chlorine impurity. Alkali bromides account for an important proportion of the bromine produced. They cannot be made by the action of caustic soda on bromine, since hypobromites and bromates are produced also. The van der Meulen process involves treating bromine with potassium carbonate in the presence of ammonia.

$$3K_2CO_3 + 3Br_2 + 2NH_3 \rightarrow 6KBr + N_2 + 3CO_2 + 3H_2O$$
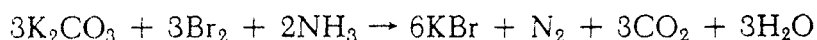
IODINE

HISTORICAL AND RAW MATERIALS. It was in 1811 that Courtois, a saltpeter manufacturer of Paris, obtained a beautiful violet iodine vapor from the mother liquors left from the recrystallization of certain salts. Iodine was later found to exist almost universally in nature. It is present as iodates (0.05 to 0.15%) in the Chilean nitrate deposits. It occurs in seawater, from

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[6]See CPI 2 for description; *Chem. Met. Eng.* 46 771 (1939); ECT. 3d ed., vol. 4, 1978. p. 226.

[7]For flowchart, see ECT, 2d ed., vol. 3, 1964, p. 760.

which certain seaweeds extract and concentrate it within their cells. Iodine has been made from these weeds by the kelp-burning process,[8] which has been practiced for years in Scotland, Norway, Normandy, and Japan. The present sources of the element, as far as the United States is concerned, however, are the nitrate fields of Chile, brine wells in Michigan, Oklahoma, and Japan, involving a total consumption of about 3900 t/year.

USES AND ECONOMICS. In the United States all but 9 percent of the iodine used is converted directly to chemical compounds.[9] The single largest use, 41 percent of the total, is for organic compounds; 21 percent is used for potassium iodide, 9 percent for sodium iodide, and 20 percent for other inorganic compounds. Iodine is used as a catalyst in the chlorination of organic compounds and in analytical chemistry for determination of the so-called *iodine numbers* of oils. Iodine for medicinal, photographic, and pharmaceutical purposes is usually in the form of alkali iodides, prepared through the agency of ferrous iodide. In addition to the above, the element is also employed in the manufacture of certain dyes and as a germicide. Simple iodine derivatives of hydrocarbons, such as iodoform, have an antiseptic action. Organic compounds containing iodine have been used as rubber emulsifiers, chemical antioxidants, and dyes and pigments. For years, Chilean-produced iodine dominated the market and controlled the price, which was set at $10 per kilogram. Upon development of the iodine from oil well brines in the southwestern United States, the price of iodine was reduced to approximately $4.80 per kilogram. Japan has recently become the world's largest iodine producer. In 1971 Japan produced more than three times the amount produced by Chile, and in 1980 over 50 percent of the world's total production. The United States produces less than 30 percent of the amount it uses. The price in 1981 was $15.90 per kilogram. Five of the 18 iodine manufacturing plants in Japan have been built since 1970. Ecological problems may seriously affect their long-term output as ground control and waste disposal regulations become more strict, but at least one of the companies has plants that satisfy environmental requirements.

FLUORINE
AND FLUOROCHEMICALS

Fluorine, a pale greenish-yellow gas of the halogen family, is the most chemically active nonmetal element. It occurs in combined form and is second only to chlorine in abundance among the halogens. The chief fluorine-containing minerals of commercial significance are fluorspar, fluorapatite (see superphosphates), and cryolite.

HISTORICAL. Fluorine was discovered by Scheele in 1771 but it was not until 1886 that it was isolated by H. Moissan, after more than 75 years of intensive effort by many experimenters. The Freon refrigerants developed in 1930 fostered the commercial development of anhydrous hydrofluoric acid and stimulated the growth of this new industry, which came into its own at the beginning of World War II,[10] largely because of the demands for UF_6 for isotope separation and for Freons.

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[8]Dyson, Chemistry and Chemotherapy of Iodine and Its Derivatives, *Chem. Age* 22 362 (1930).

[9]*Minerals Yearbook 1980*, vol. 1, Dept. of the Interior, 1981, p. 937; *Chem. Week* 127 (20) 44 (1980); *Chem. Eng. News* 60 (24) 12 (1982).

[10]Finger, Recent Advances in Fluorine Chemistry, *J. Chem. Ed.* 28 49 (1951); ECT, 3d ed., vol. 10, 1980, p. 630.

USES AND ECONOMICS. Elemental fluorine is costly and has comparatively limited usage. The element is employed in making sulfur hexafluoride (SF_6) for high-voltage insulation and for uranium hexafluoride. Fluorine is used directly or combined with higher metals (cobalt, silver, cerium, etc.) and halogens (chlorine and bromine) for organic fluorinations and the growing production of fluorocarbons. The largest production of fluorine compounds is that of hydrofluoric acid (anhydrous and aqueous), used in making "alkylate" for gasoline manufacture and Freon for refrigerants and aerosol cans. It is also employed in the preparation of inorganic fluorides, elemental fluorine, and many organic fluorine- and non-fluorine-containing compounds. Aqueous hydrogen fluoride is used in the glass, metal, and petroleum industries and in the manufacture of many inorganic and acid fluorides. Three of the most unusual plastics known (Chap. 34) are Teflon, a polymerization product of tetrafluorethylene, and Kel F and Fluorothene, products formed by the polymerization of chlorofluorethylenes.

The production of hydrofluoric acid has increased rapidly to keep pace with these varied and expanding uses.[11] In 1939, 6678 t was produced, in 1963, 117,045 t, and in 1981, 328.000 t. Hydrofluoric acid sells for $1.23 per kilogram in the anhydrous form (in tank cars) and $1.58 per kilogram as a 70 percent solution (in drums). About 42 percent of the hydrogen fluoride produced is used to prepare fluorocarbons, and one-third of the total goes to the aluminum industry, where synthetic cryolite, sodium aluminum fluoride, is a major constituent of the electrolyte. It is also consumed in the melting and refining of secondary aluminum. Other uses of hydrofluoric acid are found in the metals and petroleum industries.

MANUFACTURE. *Fluorine gas* is generated by the electrolysis of KHF_2[12] under varying conditions of temperature and electrolyte composition.

Both *aqueous* and *anhydrous hydrofluoric acid* are prepared in heated kilns by the following endothermic reaction:

$$CaF_2 \text{ (fluorspar)} + H_2SO_4 \rightarrow CaSO_4 + 2HF$$
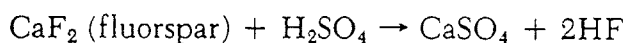
The hot, gaseous hydrogen fluoride is either absorbed in water or liquefied; refrigeration is employed to obtain the anhydrous product needed for fluorocarbon manufacture and other uses. Although hydrofluoric acid is corrosive, concentrations of 60% and above can be handled in steel at lower temperatures; lead, carbon, and special alloys are also used in the process equipment.

FLUOROCARBONS. These are compounds of carbon, fluorine, and chlorine with little or no hydrogen. Fluorocarbons containing two or more fluorines on a carbon atom are characterized by extreme chemical inertness and stability. Their volatility and density are greater than those of the corresponding hydrocarbons. More than 360×10^6 kg of fluorocarbons was produced in 1980: Refrigerants consumed 46 percent; foam blowing agents, 20 percent; solvents, 16 percent; fluoropolymers, 7 percent; and aerosol propellants less than 1 percent.[13]

Prior to 1974 aerosol propellants were the major (52 percent) end use market of fluorocarbons. In 1974 scientists at the University of California at Irvine, and at the University of Michigan, hypothesized that chlorofluorocarbons used as aerosol propellants would eventually find their way to the upper atmosphere. There they would react with the ozone layer that

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[11]*Chem. Mark. Rep.* July 20, 1981.

[12]ECT, 3d ed., vol. 10, 1980, p. 644. Flow diagrams for fluorine production and liquefaction.

[13]*Chem. Mark. Rep.* Aug. 24, 1981.

shields the earth from ultraviolet rays. A reduction in the ozone layer could allow more ultra-violet rays to reach the earth, causing a change in global weather patterns and an increase in skin cancer. This hypothesis resulted in bills being introduced in Congress and in several state legislatures to prohibit the manufacture, sale, and use of aerosols containing chlorofluorocarbons. In 1975 Oregon passed such a bill. Study committees were formed to determine the actual effect of these compounds on the ozone layer, but the "scare" caused a sharp decrease in the number of aerosol containers filled with fluorocarbons in 1976 as compared with 1974. In 1978 the Environmental Protection Agency banned the use in aerosol containers. However, only three other countries have banned fluorocarbon use for this purpose. In addition, new studies are casting doubt upon the original assumption that fluorocarbons alone are responsible for depletion of the ozone layer of the earth's atmosphere.[14]

The major use for refrigerants takes 46 percent of the production, and the remainder goes into over 100 different important applications, including plastics, films, elastomers, lubricants, textile-treating agents, solvents, and fire extinguisher products. Fluorocarbons are made from chlorinated hydrocarbons by reacting them with anhydrous hydrogen fluoride, using an antimony pentachloride catalyst. The fluorocarbons trichlorofluoromethane, dichlorodifluoromethane, and chlorodifluoromethane compose 90 percent of fluorocarbon production.

$$CCl_4 + HF \xrightarrow{SbCl_5} CCl_3F + HCl$$

$$CCl_4 + 2HF \xrightarrow{SbCl_5} CCl_2F_2 + 2HCl$$
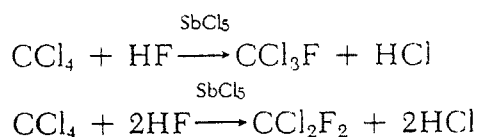
Difluoromonochloromethane is made by substituting chloroform for the carbon tetrachloride:

$$CHCl_3 + 2HF \xrightarrow{SbCl_5} CHClF_2 + 2HCl$$
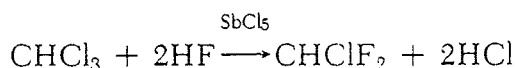
The fluorocarbon process shown in Fig. 20.4 may be divided into the following coordinated sequences:

Anhydrous hydrogen fluoride and carbon tetrachloride (or chloroform) are bubbled through molten antimony pentachloride catalyst. These reactions are slightly endothermic and take place in a steam-jacketed atmospheric pressure reactor at 65 to 95°C.

The gaseous mixture of fluorocarbon and unreacted chlorocarbon is distilled to separate and recycle the chlorocarbon to the reaction.

Waste hydrogen chloride is removed by water absorption.

The last traces of hydrogen chloride and chlorine are removed in a caustic scrubbing tower.

FLUOROSILICATES OR SILICOFLUORIDES. An important potential source of fluorine compounds is phosphate rock which, in processing, yields recoverable fluorine by-products. In 1962 Stauffer Chemical announced plans for the production of hydrogen fluoride from this source.[15] The wet process for superphosphates (Chap. 1) evolves a toxic gaseous mixture of

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[14]Fluorocarbons Are an Issue Again, *Chem. Bus.* June 1, 1981; *Chem. Week* 130 (5) 16 (1982).
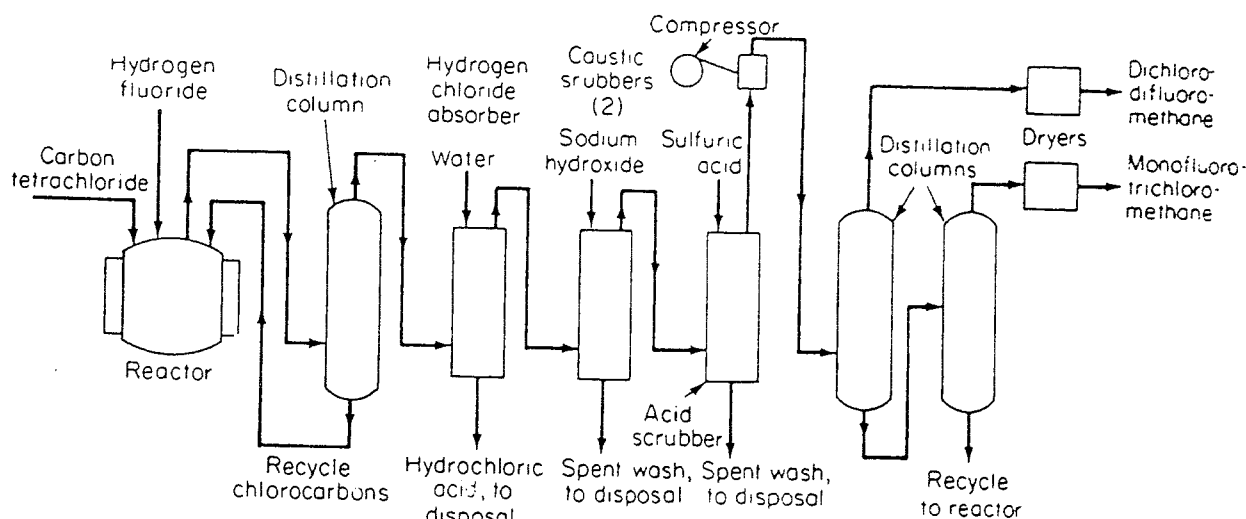
[15]See Chap. 16, Phosphorus Industries.

Fig. 5 .4. Fluorocarbon production. [*Chem. Eng.* 72 (2) 93 (1965).]

fluorine compounds, predominantly silicon tetrafluoride, hydrofluoric acid, and fluorosilicic acid (H_2SiF_6). This mixture is passed through water-absorption towers, yielding fluorosilicic acid and a silica precipitate. The H_2SiF_6 liquor is concentrated to commercial strengths (generally 30 to 35%) by recycling or distillation. An important use for this acid is in the fluoridation of municipal water supplies and also in the brewing industry as a disinfectant for copper and brass vessels. It is also employed as a preservative, in electroplating, as a concrete hardener, and in the manufacture of silicofluoride salts. The most common salt, *sodium silicofluoride* (Na_2SiF_6), is prepared by the reaction of sodium chloride or soda ash on the acid. It is used as an insecticide, laundry sour, fluxing and opacifying agent, and protective agent in the casting of light metals. Other salts such as ammonium, magnesium, zinc, copper, and barium are also prepared by neutralization and find many uses in industry.

ALUMINA

USES AND ECONOMICS. Large quantities of alumina are produced yearly for the manufacture of metallic aluminum (Chap. 14). In 1980, 90 percent of the raw material, *bauxite*, was obtained from foreign sources.[16] Jamaica, Haiti, the Dominican Republic, Surinam, Guyana, Guinea, and Australia are the countries from which the United States imports this bauxite. Total consumption was 15.6×10^6 t, about 96 percent of this going to alumina production; smaller uses include abrasives, chemical manufacture, refractories, and ceramic fibers.

MANUFACTURE. Figure 5 .5 shows the essential procedure in the production of alumina, which may be divided into the following steps:

Bauxite, a mineral containing about 55% aluminum oxide and less than 7% silica, is crushed and wet-ground to 100-mesh.

The finely divided bauxite is dissolved under pressure and heat in Bayer digesters with concentrated spent caustic soda solution from a previous cycle and sufficient lime and soda

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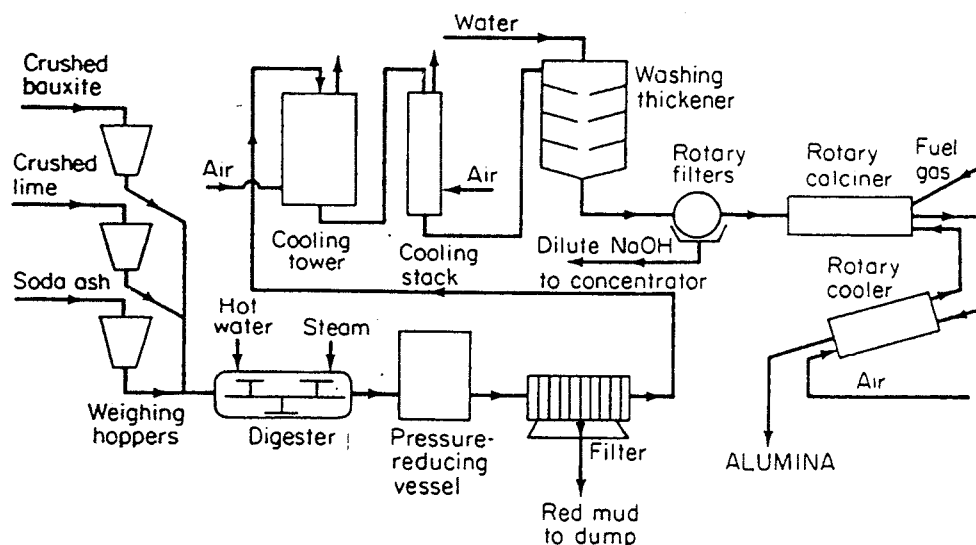[16]*Minerals Yearbook 1980*, vol. 1, Dept. of the Interior, 1981, p. 113.

Fig. 5 .5. Refining of aluminum.

ash. Sodium aluminate is formed, and the dissolved silica is precipitated as sodium aluminum silicate.

The undissolved residue (red mud) is separated from the alumina solution by filtration and washing and sent to recovery. Thickeners and Kelly or drum filters are used.

The filtered solution of sodium aluminate is hydrolyzed to precipitated aluminum hydroxide by cooling.

The precipitate is filtered from the liquor and washed.

The aluminum hydroxide is calcined by heating to 980°C in a rotary kiln.

The alumina is cooled and shipped to reduction plants.

The dilute caustic soda filtered from the aluminum hydroxide is concentrated for reuse.

The red mud may be reworked for recovery of additional amounts of alumina.

Several other processes for producing alumina based on ores other than bauxite have been announced. A Mexican process (called the U.G. process) uses alunite, a hydrous sulfate of aluminum and potassium. It is claimed to be capable of producing 99% pure alumina from alunite containing only 10 to 15% alumina, compared with bauxite which assays 50% alumina. The alunite is crushed, dehydroxylated by heating to 750°C, ground, and treated with aqueous ammonia. Filtration removes the alumina hydrate, and potassium and aluminum sulfates are recovered from the filtrate and sold as fertilizer. The alumina hydrate is treated with sulfur dioxide gas, and the resulting aluminum sulfate converted to alumina by heating in a kiln.[17]

The French Pechiney-Ugine Kuhlmann process treats clays and shales with concentrated sulfuric acid. Hydrochloric acid is added during the crystallization step to form aluminum chloride which crystallizes readily. Much raw material must be handled, because the clays and shales have a lower alumina content than bauxite.[18]

Other methods involve the treatment of clays with nitric acid (Bureau of Mines) and the continuous electrolysis of aluminum chloride (Alcoa).

[17]Parkinson, Alumina From Alunite, *Eng. Min. J.* 175 (8) 75 (1974).

[18]Alumina Producers Look to Alternate Raw Materials, *Chem. Eng.* 81 (9) 98 (1974); Patterson, Aluminum from Bauxite, Are There Alternatives? *Am. Sci.* 65 345 (1977); Barclay and Peters, New Sources of Alumina, *Min. Cong. J.* 62 (6) 29 (1976).

ALUMINUM SULFATE
AND ALUMS

The manufacture of alums entails just one step additional to the aluminum sulfate process. This, along with the fact that the uses of aluminum sulfate and alums are similar and the compounds are largely interchangeable, justifies their concurrent discussion. The term *alum* has been very loosely applied. A true alum is a double sulfate of aluminum or chromium and a monovalent metal (or a radical, such as ammonium). Aluminum sulfate is very important industrially and, although it is not a double sulfate, it is often called either alum or paper-makers' alum. Alum has been known since ancient times. The writings of the Egyptians mention its use as a mordant for madder and in certain medical preparations. The Romans employed it to fireproof their siege machines and probably prepared it from alunite, $K_2Al_6(OH)_{12}(SO_4)_4$, which is plentiful in Italy.

USES AND ECONOMICS. Alums are used in water treatment and sometimes in dyeing. They have been replaced to a large extent in these applications by aluminum sulfate, which has a greater alumina equivalent per unit weight. Pharmaceutically, aluminum sulfate is employed in dilute solution as a mild astringent and antiseptic for the skin. The most important single application of it is in clarifying water, more than half of the total amount manufactured being so consumed. Sodium aluminate, which is basic, is sometimes used with aluminum sulfate, which is acid, to produce the aluminum hydroxide floc:

$$6NaAlO_2 + Al_2(SO_4)_3 + 12H_2O \rightarrow 8Al(OH)_3 + 3Na_2SO_4$$
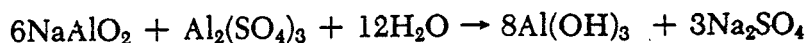
Second in importance is the application of aluminum sulfate in the sizing of paper. It reacts with sodium resinate to give the insoluble aluminum resinate. For the sizing of paper, aluminum sulfate must be free from ferric iron, or the paper will be discolored. The ferrous ions do not harm, since they form a soluble, practically colorless resinate, which, however, represents a loss of resinate. A small amount of aluminum sulfate is consumed by the dye industry as a mordant. Other uses include chemical manufacturing, concrete modification, pharmaceutical preparations, soaps and greases, fire extinguishing solutions, tanning, and cellulosic insulation. Soda alum, or aluminum sulfate, is used in some baking powders. In 1981, 1,085,000 t of commercial aluminum sulfate was produced.[19]

MANUFACTURE. Practically all alums and aluminum sulfate are now made from bauxite by reaction with 60°Bé sulfuric acid. However, potash alum was first prepared from alunite by the ancients. Other possible sources of alums are shales and other alumina-bearing materials such as clay. Figure 5.6 illustrates the manufacture of aluminum sulfate.[20] The bauxite is ground until 80 percent passes 200 mesh; next it is conveyed to storage bins. The reaction occurs in lead-lined steel tanks, where the reactants are thoroughly mixed and heated with the aid of agitators and live steam. These reactors are operated in series. Into the last reactor barium sulfide is added in the form of black ash to reduce ferric sulfate to the ferrous state and to precipitate the iron. The mixture from the reactors is sent through a series of thickeners, operated countercurrently, which remove undissolved matter and thoroughly wash the

[19]*Chem. Eng. News* **60** (24) 33 (1982).

[20]*Chem. Eng. Prog.* **70** (1) 55 (1974) (alum flowchart of Allied Chemical Corp.); ECT, 3d ed., vol. 2, 1978, p. 218.
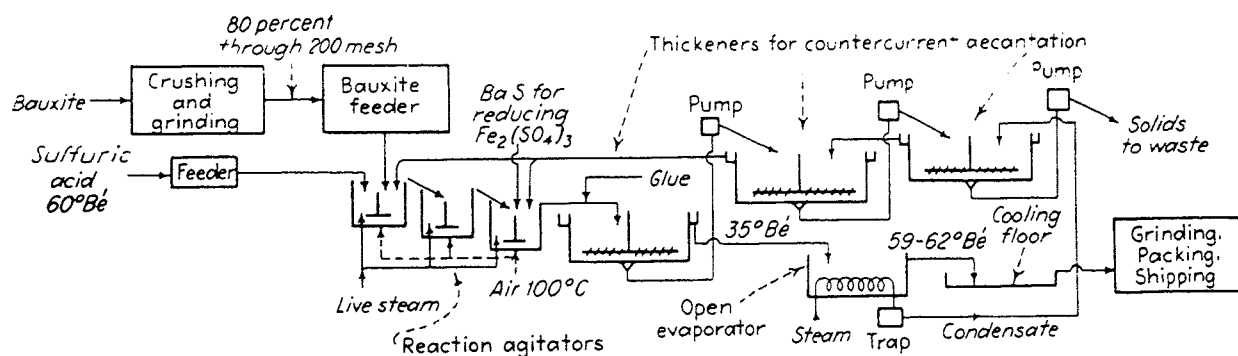
In order to produce 1 t of 17% Al_2O_3 "alum," the following materials and utilities are required:

Bauxite (55% Al_2O_3)	338 kg	Coal (steam)	380 kg
H_2SO_4 (60°Bé)	575 kg	Electricity	115 MJ
Black ash (70% BaS)	6.6 kg	Direct labor	1.6 work-h
Flake glue	0.2 kg		

Fig. 5 .6. Manufacture of aluminum sulfate by the Dorr process. NOTE: A common variation of this flow sheet is to use a battery of combined reaction and settling tanks instead of agitators and thickeners.

waste so that, when discarded, it will contain practically no alum. The clarified aluminum sulfate solution is concentrated in an open, steam-coil heated evaporator from 35 to 59 or 62°Bé. The concentrated liquor is poured into flat pans, where it is cooled and completely solidified. The solid cake is broken and ground to size for shipping. Another slightly modified procedure uses, instead of reactors and thickeners, combined reaction and settling tanks. The Dalecarlia rapid-sand filter plant, which supplies water to Washington, D.C., makes its own filter alum. In this case concentration of liquor would be an unnecessary expense; therefore the aluminum sulfate is made and used in a water solution. To make the various true alums, it is necessary only to add the sulfate of the monovalent metal to the dilute aluminum sulfate solution in the proper amount. Concentration of the mixed solution, followed by cooling, yields alum crystals.

ALUMINUM CHLORIDE

Aluminum chloride is a white solid when pure. On heating it sublimes and, in the presence of moisture, anhydrous aluminum chloride partly decomposes with the evolution of hydrogen chloride. This salt was first prepared in 1825 by Oersted, who passed chlorine over a mixture of alumina and carbon and condensed the vapors of the aluminum chloride formed. Essentially the same process is used today in the commercial preparation of aluminum chloride. The price in 1913 was $3.30/kg and the present price is $1.00/kg in carload lots.

USES. Since modern methods of manufacture have reduced the price of aluminum chloride, it has found application in the petroleum industries and various phases of organic chemistry technology. Aluminum chloride is a catalyst in the alkylation of paraffins and aromatic hydrocarbons by olefins and also in the formation of complex ketones, aldehydes, and carboxylic acid derivatives. In 1980, 25,000 t of anhydrous aluminum chloride was manufactured. Anhydrous aluminum chloride is manufactured primarily by the reaction of chlorine vapor on molten aluminum.[21] Chlorine is fed in below the surface of the aluminum, and the product

sublimes and is collected by condensing. These air-cooled condensers are thin-walled, vertical steel cylinders with conical bottoms. Aluminum chloride crystals form on the condenser walls and are periodically removed, crushed, screened, and packaged in steel containers.

COPPER SALTS

Copper sulfate[22] is the most important compound of copper, and more than 29000 t was produced in 1976. Commonly known as *blue vitriol*, it is prepared by the action of sulfuric acid on cupric oxide or sulfide ores. Its poisonous nature is utilized in the fungicide Bordeaux mixture, which is formed upon mixing copper sulfate solution with milk of lime. Copper sulfate is added to water reservoirs occasionally to kill algae. It is employed in electroplating and finds minor applications as a mordant, germicide, and agent in engraving. Certain copper compounds are added to antifouling paints used on ship bottoms.

MOLYBDENUM COMPOUNDS

Although the largest use for molybdenum lies in metallurgy, chemical applications make up a rapidly growing segment of diversified uses. Approximately 10 percent of the total molybdenum production of over 51,000 t/year goes into compounds.[23] Molybdenum disulfide is dispersed in greases and oils for lubrication; in volatile carriers it is used to form dry coatings of lubricant. Sodium molybdate is an especially effective corrosion inhibitor on aluminum surfaces and is dissolved in cooling solutions to protect aluminum motor blocks in automobiles.[24] Molybdenum salts used as catalysts include cobalt molybdate for hydrogen treatment of petroleum stocks for desulfurization, and phosphomolybdates to promote oxidation. Compounds used for dyes are sodium, potassium, and ammonium molybdates. With basic dyes, phosphomolybdic acid is employed. The pigment known as *molybdenum orange* is a mixed crystal of lead chromate and lead molybdate. Sodium molybdate, or molybdic oxide, is added to fertilizers as a beneficial trace element. Zinc and calcium molybdate serve as inhibitory pigments in protective coatings and paint for metals subjected to a corrosive atmosphere. Compounds used to produce better adherence of enamels are molybdenum trioxide and ammonium, sodium, calcium, barium, and lead molybdates. The mineral raw material is molybdenite, which, by roasting, furnishes a technical grade of molybdenum trioxide of 80 to 90% purity.

BARIUM SALTS

The most common naturally occurring barium compounds are the mineral carbonate, or witherite, which is fairly abundant in England, and the sulfate, or barite, which is common in certain sections of the United States. The most important domestic source of barite is Nevada, but there are mines in many other states. West Germany has become the major

[22]ECT, 3d ed., vol. 7, 1979, p. 97.

[23]*Minerals Yearbook 1980*, vol. 1, Dept. of Interior, 1981, p. 103.

[24]Vukasovich, Sodium Molybdate Corrosion Inhibition, *Lubr. Eng.* 36 (12) 709 (1980); *Mod. Paint Coat.* 70 (2) 45 (1980).